

Relative Efficacy of a Drinking-Water Treatment Residual and Alum in Reducing Phosphorus Release from Poultry Litter

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Abstract: Amending poultry litter with alum (aluminum sulfate) effectively reduces soluble phosphorus (P) concentrations, but the practice can be expensive. Aluminum (Al)-based drinking-water treatment residuals (WTRs) can be obtained free of charge and are enriched in Al hydr(oxides) that make them efficient P sorbents. Substituting Al-WTRs for alum would be a cost-effective practice to reduce soluble P in manures when compared with alum-only use. The research studied the reductions in soluble P, Al, and total organic carbon (TOC) concentrations in suspensions prepared by mixing variable Al-WTR and alum rates (0 to 25% by weight) with poultry litter. Suspensions were maintained at pH of 6.5 during the sorption step, and allowed to react up to 50 d, without shaking. On a per-mole of oxalate-extractable Al basis, the Al-WTR was nearly as effective as alum in reducing P release. Increasing mixed alum/WTR mass loads resulted in greater soluble P reduction, simply due to increased molar Al/P ratios. Contact time did not significantly influence soluble P reduction. Two significant advantages of Al-WTRs compared to alum indicated by this study are cost effectiveness and significantly less release of dissolved Al. Soluble Al and TOC concentrations were least for suspensions with the lowest soluble P levels, suggesting that P was removed from solution as an organo-Al-P amorphous phase. The amount of P desorbed from the mixtures decreased to <1% with increasing molar Al/P ratios ≥ 1 . Results suggest that Al-WTR application with

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or without alum can reduce soluble P in poultry litter; however, field validation of the amendment effectiveness is needed.

Keywords: Residuals, soil amendments, waste management

INTRODUCTION

There is an increasing public demand to reduce phosphorus (P) transport to water bodies at risk of eutrophication from agricultural-P inputs, including land application of animal wastes. Animal wastes contain considerable amounts of P that have a great potential for surface runoff or leaching toward water bodies. Extensive efforts have been focused on finding ways to reduce soluble P in animal wastes. Techniques used to reduce soluble P are divided into three main categories: physical (electrodialysis, reverse osmosis), biological, and (most commonly) chemical methods.

A conventional chemical method to reduce soluble P in animal wastes is the application of a chemical coagulant, like alum (aluminum sulfate) (Moore et al., 1996; Lefcourt and Meisinger, 2001; Sims and Luka-McCafferty, 2002; Dou et al., 2003). Alum has been applied to soils high in P, such as those heavily amended with poultry litter (Shreve et al., 1995; Self-Davis et al., 1998). Alum has also been applied to wetlands to reduce P release from sediments. Alum additions (1.2% alum by wt.) minimized P release from a constructed wetland (Ann et al., 2000).

The multicomponent chemical composition of manure poses a challenge to effective characterization of P chemistry in amended systems, even with advanced spectroscopic techniques. X-ray absorption near-edge structure spectroscopy (XANES) application to alum-treated poultry litter suggested that reduction in soluble P resulted from precipitation of amorphous Al hydroxide followed by P adsorption on the aluminum (Al) hydroxide (Peak et al., 2002). However, the P solid phase reference database used by the researchers did not include organo-Al-P spectra that could be compared with the sample spectra (Peak et al., 2002).

The role of dissolved organic carbon (DOC) in regulating P sorption remains incompletely understood. Increased DOC in manure suspensions may bind to Al^{3+} , creating soluble metal-organic complexes. Recent work with ^{31}P -NMR spectroscopy discussed the possibility of organo-Al-P association in alum-treated poultry litter (Hunger et al., 2004). Phosphorus chemical shifts were influenced by cations complexed with P (Hunger et al., 2004). Inorganic cation-P bonding shows pronounced, sharp chemical shifts, whereas chemical environments that contain organically complexed cations exhibit broad P chemical shifts that are difficult to interpret (Hunger et al., 2004).

The established effectiveness of alum in reducing soluble P concentrations in poultry manure is accompanied by a significant economic cost.

A typical broiler house needs 1.8 tons of alum per growing season, or 0.1 kg bird^{-1} (Moore, 1998). Assuming a value of $\$2.6 \text{ kg}^{-1}$ alum, then $\sim \$4,700$ is needed to apply the optimum rate of alum. Not included in the economic analysis is the cost involved with use of lime, or sodium aluminate that is occasionally applied to bring the pH of the alum solution close to neutral levels.

Drinking-water treatment residuals (WTRs) are the by-products of the drinking water purification process in treatment plants, and are potential alternatives to alum as a P-mitigating amendment. Drinking-WTRs are usually disposed of in landfills, and can be obtained at minimal, or no cost from drinking-water treatment plants. Drinking-WTRs are amorphous masses of Al or Fe hydr(oxides) that originate from flocculant (Al or iron (Fe) salts) additions made during the drinking-water purification (O'Connor et al., 2001). These residuals are herein referred to as Al-WTRs (use of Al salt) or Fe-WTRs (Fe salt). Synthetic polyelectrolytes like surfactants and polymers are used in conjunction with inorganic flocculants such as alum to promote settling of particles in water treatment plants (Hiemenz and Rajagopalan, 1997; Ozacar and Sengil, 2003).

Aluminum-WTRs are rich in Al, suggesting that they could have a similar effect to alum in reducing poultry litter soluble P concentrations. Large amounts of amorphous Al hydr(oxides) in Al-WTRs make them efficient P sorbents (O'Connor and Elliott, 2000). Use of WTRs is an emerging practice to reduce soluble P in systems high in P (O'Connor and Elliott, 2000; Peters and Basta, 1996; Haustein et al., 2000; Elliott et al., 2002). Oxalate-extractable Al and the Langmuir P sorbing maxima of 21 tested Al-WTRs were the key parameters that explained the significant reduction in runoff-P from WTR-amended soils treated with poultry litter (Dayton et al., 2003). Partial or complete substitution of Al-WTRs for alum may be a cost-effective practice to reduce soluble P in animal waste, if Al-WTR efficacy is similar to that of alum. Complete substitution of Al-WTRs for alum could be practiced in cases of year-around, abundant WTR availability. Conversely, alum could substitute for Al-WTR when the Al-WTR supplies are limited.

Preliminary work in our lab has shown that the same Al-WTR used in this study exhibited fast and huge P sorption capacity ($> 10 \text{ g kg}^{-1}$) against inorganic P solutions in batch experiments. On the contrary, the effectiveness of the same Al-WTR to reduce soluble P concentrations in dairy manure-amended soils was reduced in the presence of dissolved or colloidal organics (Lane, 2002). This led us to test and compare the Al-WTR with alum's effectiveness in reducing soluble P concentrations in organic waste (poultry litter) suspensions.

The mechanism by which P is immobilized by WTRs differs from that of alum P fixation. Alum is soluble in water and P inactivation occurs via a formation of an Al-P precipitate. Drinking-WTR particles are essentially insoluble in water. Rather, they are rigid particles with significant

microporosity specific surface area (Markis et al., 2005). Intraparticle P diffusion in the porous WTR structure was the main mechanism responsible for P sorption by WTRs (Markis et al., 2004). The different P retention mechanisms possible prompted us to test the potential synergistic/antagonistic effects of combining alum with Al-WTR on the reduction of soluble P in poultry litter.

Knowledge of the relative efficacy of Al-WTRs and alum in reducing soluble P in animal wastes is required if Al-WTRs are to ultimately be used as cost effective and environmentally friendly alternatives to alum. No work has been conducted on the combined use or comparison between Al-WTRs and alum as means to reduce soluble P in poultry litter. The objectives of this study were 1) to compare alum versus Al-WTR effectiveness in reducing soluble P concentrations in poultry litter and 2) to evaluate evidence for the formation of an amorphous organo-Al-P phase rather than a simple inorganic Al-P phase in alum/Al-WTR treated poultry litter.

MATERIALS AND METHODS

General Characteristics

Ten grams (dry weight equivalent) of composted poultry litter were immersed in 100 mL of 0.01 M KCl and left to equilibrate for 1 day. Alum [$\text{Al}_2(\text{SO}_4)_3 \cdot 14\text{H}_2\text{O}$, A.C.S. grade, Fisher Scientific, Inc., Fair Lawn, NJ] and an Al-WTR from the Bradenton, FL, water treatment plant were added to litter suspensions in different weight-based ratios to give a total amendment concentration range of 0 to 25% of dry litter weight. The Al-WTR was sampled directly from an evaporation pond, air-dried, and passed through a 2-mm sieve. The pH of a 0.01 M KCl solution of the litter and the WTR was measured after 40 d reaction (1 : 10 solid : solution ratio).

Determination of percentage solids was performed by drying the materials at 105°C (Sparks, 1996). KCl-extractable P was measured at a ratio of 1 : 10 in a 0.01 M KCl solution after 40 d. Total C and N were determined by combustion at 1010°C using a Carlo Erba NA-1500 CNS analyzer. The WTR and the litter were analyzed for total-recoverable P, Fe, and Al by ICP following digestion according to the EPA Method 3050B (USEPA, 2000). Oxalate-extractable P, Fe, and Al of the amendments and the suspensions were determined by ICP after extraction at a 1 : 60 solid : solution ratio (McKeague et al., 1971). Alum is a well-characterized coagulant and was not included in the initial characterization. Powder XRD analyses of the WTR/alum/litter mixtures were conducted using monochromatic $\text{CuK}\alpha$ radiation at 35 kV and 20 mA. The 2θ diffraction angle (2° to 70°) was scanned at a rate of $2^\circ (2\theta) \text{ min}^{-1}$.

The calculated Al/P molar ratios of the suspensions were based on the oxalate-extractable P value of the litter, the total Al concentration of alum,

and the oxalate-extractable Al concentration of the Al-WTR. Aluminum in alum was assumed to be 100% extractable with oxalate. Molar Al/P ratios ranged from 0.34 to 1.32. Oxalate-extractable WTR-P was ignored since it was low (2.98 g kg^{-1}), and not labile (data not shown), when compared with the litter oxalate-P. Use of oxalate P to determine molar ratios was considered more relevant than using total P, since total P, at least in animal wastes, does not reflect the material's P availability (Burns et al., 2001). The high P sorbing capacity ($\geq 10 \text{ g P kg}^{-1}$ WTR) of the Al-WTR was determined previously (Makris, 2004) by constructing a P sorption isotherm (23 C) following incubation of the Al-WTR with inorganic P solutions for 10 d.

Central Composite Design

A central composite design (Mason et al., 1989) was used to investigate the main effects and interactions of combining alum and an Al-WTR (Fig. 1). WTR and alum weight loads and contact time were the three factors investigated. Five levels of each factor were used to encompass a range of alum concentrations used to reduce soluble P from poultry litter (Table 1). Synergistic or antagonistic effects of alum and the Al-WTR on soluble P levels in litter suspensions were evaluated in experimental units prepared using combinations of the two sorbents (Table 2). The central composite design has been widely used in the fields of statistics and engineering (Mason et al., 1989; Christmas et al., 2002) but not as extensively in agricultural research. The major advantage of the central composite design is that three variables at five levels can be evaluated with a limited number (Makris et al., 2004) of experimental units. The central composite design identifies the main and interaction effects of the variables, which are not obtained by analyzing one

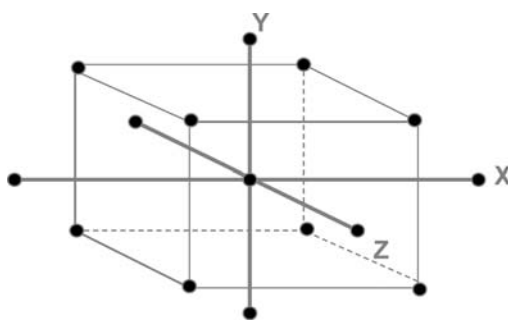


Figure 1. Three-dimensional geometric representation of the experimental runs (dots) used in the central composite design. The dot in the center of the cube represents the experimental run that corresponds to the mid-point level of each factor. X, Y, and Z axes represent the three tested factors.

Table 1. The factors used in the central composite design, five levels each. The equation below is the quadratic polynomial used to describe the main and interactive effects of WTR, alum, and time on the amounts of reduced KCl-P in poultry litter

Factors	Levels				
WTR (%)	0	5.1	12.5	20.0	25.5
Alum (%)	0	5.1	12.5	20.0	25.5
Time (days)	0.44	10.5	25.5	40	50

$$y = a_0 + \text{WTR} + \text{alum} + \text{time} + \text{WTR}^2 + \text{alum}^2 + \text{time}^2 + \text{WTR} \times \text{alum} + \text{WTR} \times \text{time} + \text{alum} \times \text{time}.$$

variable at a time. Twenty experimental units were used, consisting of combinations of the five levels for each factor. There were 14 single-run experimental units (dots), plus six replicated runs for the dot in the center of the cube (Fig. 1). The design's limited number of runs prohibits the use of traditional statistical methods such as the separation of treatment means technique.

Table 2. Central composite design structure with three factors, five levels each. The runs below represent the dots in Fig. 1. There are 14 single-run dots on the cube in Fig. 1 plus 6 replicated runs (total 20 runs) for the mid-point in the center of the cube

Run #	% WTR added	% Alum added	Time (d)
1	12.55	12.55	0.44
2	20	5.1	10.5
3	5.1	5.1	10.5
4	5.1	20	10.5
5	20	20	10.5
6	25.08	12.55	25.25
7	12.55	12.55	25.25
8	12.55	0	25.25
9	12.55	12.55	25.25
10	12.55	12.55	25.25
11	0	12.55	25.25
12	12.55	12.55	25.25
13	12.55	25.08	25.25
14	12.55	12.55	25.25
15	12.55	12.55	25.25
16	5.1	5.1	40
17	20	20	40
18	5.1	20	40
19	20	5.1	40
20	12.55	12.55	50

Phosphorus Sorption/Desorption

Amendments (alum, with or without WTR, and WTR-only) were mixed with 10 g (dry wt.) of poultry litter at a 1 : 10 solid : solution ratio in 0.01 M KCl. Potential pH effects on the magnitude of soluble P in suspensions due to pH differences between alum and WTR solutions were minimized by maintaining the pH at 6.5. The pH of the suspensions was adjusted using micro-quantities of strong acid (HCl for WTR) or base (NaOH for alum). The pH of the suspensions for all treatments, after the completion of the sorption experiment, ranged from 6.3–6.7.

The suspensions were not shaken during the equilibration period (0.4 to 50 d) to avoid WTR particle abrasion and the artificial generation of new solid surfaces. Artificial increases in specific surface area may influence the magnitude of P sorption. Suspensions were reacted for 0.4 to 50 d in an attempt to show the long-term P sorption capacity of the Al-WTR. After equilibration, the suspensions were centrifuged, and the supernatants passed through 0.22 μm filters and analyzed by ICP for P and Al. Total organic carbon (TOC) in the filtered solutions was determined using a Tekmar-Dorhman Phoenix 8000 TOC Analyzer. After the completion of the sorption step, residual materials were re-suspended in a 0.01 M KCl solution (1 : 10 solid : solution ratio) to monitor P desorption. The suspensions were reacted for 0.4 to 50 d, without shaking or pH control, then centrifuged, filtered, and analyzed for P, Al, and TOC, as described previously.

RESULTS

General Chemical Properties

The poultry litter and the Al-WTR had contrasting chemical and physical properties (Table 3). The higher moisture content (lower % solids) of the air-dried Al-WTR was due to its ability in retaining significant amounts of water into its internal surfaces. The litter C:N ratio (5.4) was less than average values (~ 10) reported in the literature (Sharpley and Moyer, 2000). The Al-WTR had a higher TOC content (162 g kg^{-1}) than the median value of 63 g kg^{-1} reported for 21 Al-WTRs (Dayton et al., 2003).

On a dry matter basis, the poultry litter had a greater P concentration (44.9 g kg^{-1}) than the 20 g P kg^{-1} average (Barnett, 1994). Total P content of the WTR (3.1 g kg^{-1}) was slightly greater than measured for another sample of the Al-WTR from Bradenton, FL (2.8 g kg^{-1}) (O'Connor and Elliott, 2000), and much greater than the median value (1.3 g kg^{-1}) reported for a host of Al-WTRs (Dayton et al., 2003). The poultry litter had little Al and Fe since calcium (Ca) is usually the dominant element (Barnett, 1994). The Al content of the WTR (92 g kg^{-1}) was within the typical range (50 to 150 g kg^{-1}) (American Society of Civil Engineers, 1996).

Table 3. Selected properties of the poultry litter and the Al-WTR (oven-dry basis)

Form	pH	% Solids	C	N	Total (g kg ⁻¹)			0.2 M Oxalate (g kg ⁻¹)		
					P	Al	Fe	P	Al	Fe
Poultry litter	7.2	74.4 ^a ± 1.2	258 ± 8.0	48 ± 0.2	44.9 ± 2.5	2.4 ± 0.3	0.4 ± 0.04	31.6 ± 1.9	0.5 ± 0.08	0.28 ± 0.03
Al-WTR	5.4	40.6 ± 1.6	162 ± 8.0	6.0 ± 0.2	3.1 ± 0.7	92 ± 5.4	6.2 ± 0.1	2.98 ± 0.02	91.1 ± 1.3	5.2 ± 0.3

^aMean of two samples ± standard deviation.

X-ray diffraction (XRD) analysis confirmed the noncrystalline nature of the WTR and litter before mixed with alum (data not shown). Oxalate P was lower than total since oxalate values represent only amorphous P forms. Poultry litter oxalate-P was 70% of the total, suggesting a high degree of P lability. Oxalate Al plus Fe for the WTR was 96% of the total Al + Fe, suggesting that highly reactive Al/Fe hydroxides make the Al-WTR a sink for P.

Reduction in KCl-Extractable Phosphorus

A 25-d reaction period was selected to present the results since this reaction time had the most replicates (of the other reaction times) in the central composite design. In addition, as we will see below, there was no significant effect of reaction time, so we focused on the 25 d data. The calculated reduction in soluble P levels was based on the KCl-extractable P concentrations measured in litter-only compared with litter suspensions treated with alum and/or WTR, at different reaction times, according to the following Eq. (1):

$$\text{Reduced P (mg kg}^{-1}\text{)} = [\text{litter-only P (mg L}^{-1}\text{)} - \text{litter} \\ + \text{sorbents P (mg L}^{-1}\text{)}] \times [\text{suspension volume (L)/mass litter (kg)}] \quad (1)$$

The sorbent-free KCl-P values in the poultry litter fluctuated somewhat with time, but there was no clear trend with time (Fig. 2). On average, the mean sorbent-free KCl-P in the litter suspensions ($\sim 5,300 \text{ mg kg}^{-1}$) was approximately 12% of the initial total P concentration ($44,900 \text{ mg P kg}^{-1}$). This percentage of soluble P in sorbent-free poultry litter agrees with published values (Peak et al., 2002).

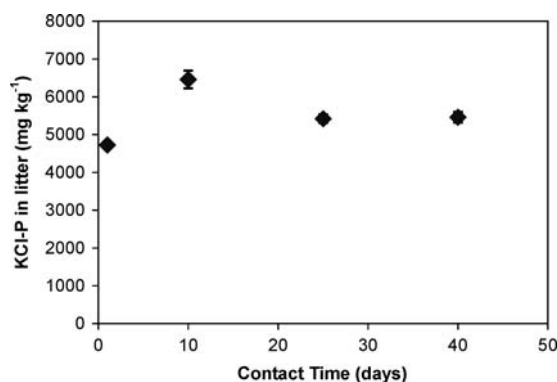


Figure 2. Kinetics of KCl-extractable P release in suspensions of poultry litter without alum or WTR in 0.01 M KCl background electrolyte. Data are the mean of two replicates and the error bars represent one standard deviation.

In the absence of competing sorbent, either Al-WTR or alum exhibited similar abilities to reduce KCl-extractable P concentrations in litter suspensions after 25 d (Table 4). Based on the ANOVA of the central composite design (Table 5), the main effects of WTR and alum, but not the contact time, were significant ($p < 0.001$). The fast reaction is understandable for the soluble alum salt (direct precipitation reaction with P), but perhaps surprising for the solid-phase WTR (P sorption is diffusion-limited). However, earlier P sorption kinetics studies using the Al-WTR and inorganic P solutions showed that 75% of the initial soluble P load (10 g kg^{-1}) was removed from solution within 1 d, and essentially no P remained in solution after 10 d (Makris, 2004). Thus, P sorption reactions were expected to be complete relatively quickly.

Poultry litter-P sorption by the Al-WTR-only experimental run in this study was relatively fast, but only 52% of the initial total soluble P concentration in poultry litter was retained, whereas previous work would suggest nearly 100% retention. The reduced effectiveness of WTR was similar to the 55% P retention in the alum-only treatment; both treatments had <0.4 Al/P molar ratios. Poultry litter suspensions contained a significant

Table 4. Reduced soluble P levels in alum/WTR treated poultry litter suspensions for all runs of the central composite design. The “control” experimental run, which corresponds to the litter-only suspension, is not included

Run #	WTR added %	Alum added %	Time (days)	Reduced KCl-P (mg kg^{-1} manure)
1	12.55	12.55	0.44	3336
2	20	5.1	10.5	4359
3	5.1	5.1	10.5	2554
4	5.1	20	10.5	5769
5	20	20	10.5	5500
6	25.08	12.55	25.25	4693
7	12.55	12.55	25.25	4492
8	12.55	0	25.25	2755
9	12.55	12.55	25.25	4105
10	12.55	12.55	25.25	4721
11	0	12.55	25.25	3024
12	12.55	12.55	25.25	4480
13	12.55	25.0	25.25	5304
14	12.55	12.55	25.25	4798
15	12.55	12.55	25.25	4637
16	5.1	5.1	40	3220
17	20	20	40	5336
18	5.1	20	40	5212
19	20	5.1	40	4587
20	12.55	12.55	50	5032

Table 5. Analysis of variance table of the central composite design. A linear equation used to fit the P sorption experimental data

Source	Sum of squares	DF	Mean square	F value	Prob > F
Model	1.34E+007	3	4.45E + 006	20.05	<0.0001
WTR	2.49E+006	1	2.49E + 006	11.23	0.0041
Alum	9.49E+006	1	9.48E + 006	42.73	<0.0001
WTR × Alum	1.37E+006	1	1.37E + 006	6.20	0.0242
Residual	3.55E+006	16	2.22E + 005		
Pure Error	3.08E+005	5	61.640		
Cor Total	1.69E+007	19			
Std. Dev.	471			R-Squared	0.79
Mean	4390			Adj R-Squared	0.75
C.V.	10.7			Pred R-Squared	0.69

Reduced KCl-P (mg kg^{-1} litter) = $1095 + 151 \times \text{WTR} (\%) + 205 \times \text{Alum} (\%) - 7 \times \text{WTR} \times \text{Alum}$.

amount of DOC (23 g C kg^{-1} litter) that was speculated to be responsible for the reduced effectiveness. Data in the literature suggest that the effectiveness of alum to reduce P in wastewater suspensions depends on the % organic C, and the forms of P present (Omoike and Vanloon, 1999).

The reduced effectiveness at the low (0.4) Al/P molar ratio treatments was overcome by increasing the Al/P molar ratios to ~ 1 by adding either sorbent individually or mixtures of the two sorbents. Greater sorbent load combinations (up to 25% load, or 1.3 Al/P molar ratios) further reduced KCl-P in the litter/sorbents suspensions to nearly 100% of the initial KCl-P values (Fig. 3). A positive quadratic correlation ($r^2 = 0.75$) between the reduced KCl-P concentrations and oxalate-extractable Al/P molar ratios was observed for all experimental runs (Fig. 3).

When the two sorbents were added in different weight-based ratios to poultry litter, different amounts of reduced KCl-P were observed (Table 3). A three-dimensional surface contour plot generated from results of the central composite design illustrates the interaction between alum and Al-WTR with respect to reduced KCl-P levels in litter, after 25 d (Fig. 4). A marginally significant ($p < 0.02$) interaction with respect to reduced KCl-P levels was found for alum and Al-WTR (Table 5). The interaction between alum and the Al-WTR is manifested at unusual and impractical sorbent application rates ($> 15\%$ by weight). At rates usually recommended ($\sim 10\%$ by weight), the interaction is not significant. The plot from the model shows a linear response of reduced soluble P levels when combining the two sorbents. The lowest sorbent combination (5:5% WTR:alum, by weight) represents the common alum application rate (10%) (Moore et al., 1996), and resulted in significant decreases in KCl-P concentrations of

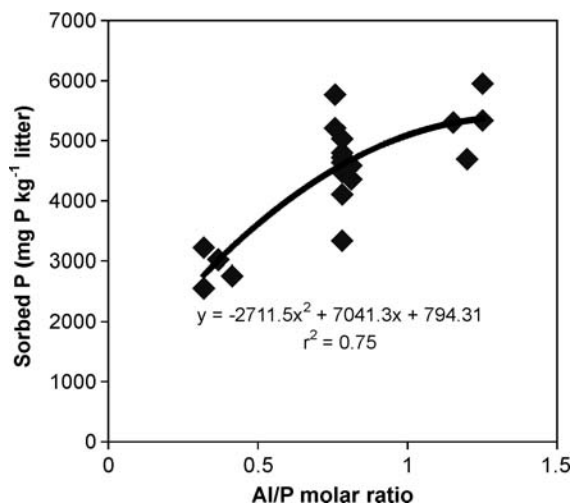


Figure 3. Relationship between sorbed P in litter suspensions and the oxalate-extractable Al/P molar ratios in all experimental runs of the central composite design. The maximum amount of soluble P in the untreated poultry litter was $\sim 5,300$ mg kg⁻¹.

2,500 mg P kg⁻¹ after 10 d and 3,200 mg P kg⁻¹ after 40 d. The increase in P sorption with time was not significant at the 95% confidence level.

Sorbent-free KCl-Al values in the poultry litter increased with time and appeared to reach equilibrium after 25 d (117 mg Al kg⁻¹ litter, data not

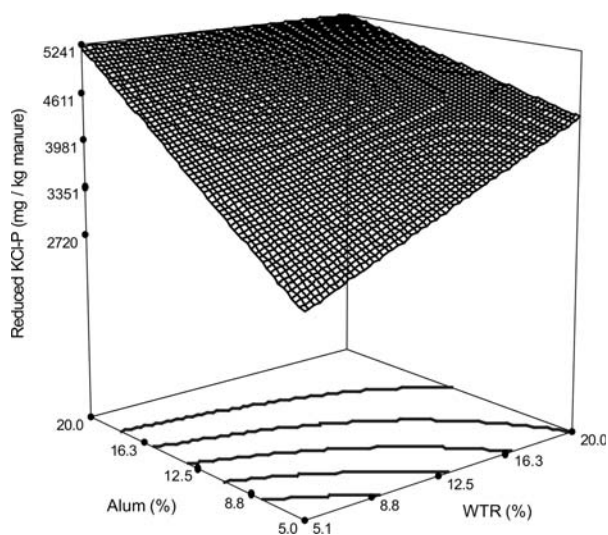


Figure 4. Three-dimensional surface contour plot of the WTR and alum effects on reducing soluble P in poultry litter suspensions, at a specific contact time (25 d).

shown). The WTR particles have limited solubility at circumneutral pH (Elliott et al., 2002) and are expected to contribute less soluble Al than litter would supply on its own. A negative linear correlation ($r^2 = 0.46$) was observed between soluble Al and the amount of reduced KCl-P in all runs (Fig. 5). After 25 d, either alum- or WTR-only/litter treated suspensions had Al residual concentrations of 5,366 and 99 mg Al kg⁻¹ sorbent, respectively. The WTR-only treated litter desorbed much less Al (99 mg Al kg⁻¹) than alum, suggesting that WTR particles are relatively insoluble with little potential of Al desorbability. Preliminary work showed that WTR particles retain their integrity and do not dissolve in circumneutral pH conditions. The potential detrimental effect of free soluble Al³⁺ concentration on plants can be minimized by using Al-WTRs, since soluble Al concentrations in WTR suspensions is typically ≤ 1 mg Al L⁻¹ (O'Connor et al., 2001).

Based on thermodynamic considerations at pH of 6.8, minimal Al³⁺ would be soluble in equilibrium with Al(OH)₃. However, alum-only treated litter suspension at pH 6.8 had the greatest soluble Al concentrations of all experimental runs, suggesting that soluble Al was likely organically complexed and not “free” Al³⁺ in solution. Potential free Al³⁺ toxicity to plants has well been documented in the literature (Barcelo et al., 1996). Although solution-complexed Al is not as nearly toxic as free Al³⁺, most people prefer to have as little soluble Al as possible. Soluble Al was minimal for Al-WTR suspensions compared with alum suspensions. The Al-WTR particles are essentially insoluble in water, and sorbed P should be stably immobilized by Al in the WTR structure, as P desorption from Al-WTR is negligible (Ippolito et al., 2003).

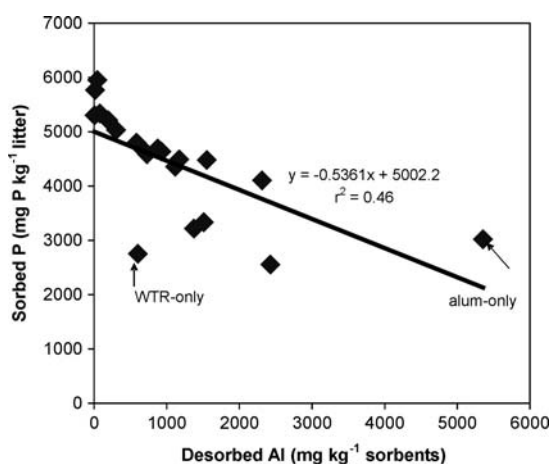


Figure 5. Relationship between Al in solution coming from alum and the WTR as a function of sorbed P in all experimental runs of the central composite design.

Total organic C was measured in supernatants of the suspensions after the completion of the P sorption experiment. The TOC was assumed to be mostly DOC since the centrifuged supernatants had passed through 0.22 μm filters. The DOC from the alum-only treated litter suspension represented the amount of DOC released from the poultry litter (TOC = 23 g C kg^{-1} litter) since alum should have had insignificant residual C levels. WTR-only treated litter had slightly, but not significantly greater (25.4 g C kg^{-1} litter plus WTR) TOC concentrations than alum-only treated litter. Median organic C content of a suite of WTRs was relatively high (63 g C kg^{-1}) (Dayton et al., 2003).

There was a negative linear correlation ($r^2 = 0.57$) between the amount of reduced KCl-P and TOC concentrations measured in solution for all experimental runs (Fig. 6). Increased TOC levels in poultry litter may have reduced the effectiveness of alum-only and WTR-only treatments (Al/P molar ratios <0.4) in reducing soluble P concentrations. Similar behavior was observed for soils amended with dairy manure (Lane, 2002), where P sorption by the same Al-WTR used in this study, was significantly reduced. The DOC from the poultry manure was an important factor for the observed decrease in P sorption (Lane, 2002).

TOC and Al concentrations in solution seem to behave in parallel, and in accordance with the amount of residual KCl-P measured in suspensions. The more soluble P retained by alum and the Al-WTR, the less Al and TOC remained in solution. However, XRD-detectable crystalline Al-P inorganic phase peaks were not present, even after 50 d of reaction of added alum and Al-WTR to poultry litter suspensions. No crystalline inorganic Al-P phase was identified in alum-treated poultry litter using synchrotron-based techniques (Peak et al., 2002).

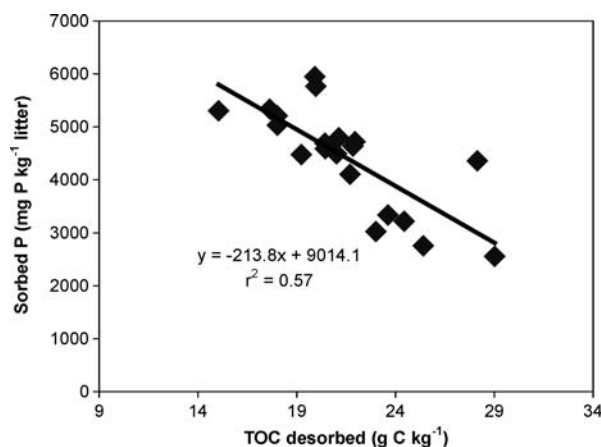


Figure 6. Relationship between TOC levels in solution coming from poultry litter and the WTR as a function of sorbed P in all runs of the central composite design.

Possibly, an amorphous organo-Al-P phase forms in the treated poultry litter suspensions. Such a moiety could be marginal with respect to a colloid-vs.-solution species distinction, and likely to pass a $0.22\ \mu\text{m}$ filter. Co-precipitation of aluminum, tannic acid, and orthophosphate produced a precipitate with very small particle size (Ng Kee Kwong and Huang, 1981). Specific surface areas of aluminum hydroxides were about five times greater in the presence of tannic acid than in the absence of the organic acid (Ng Kee Kwong and Huang, 1981). Recent work reported a close association of dissolved Al and DOC in two WTRs tested over the pH range of 2 to 12 (Prakash and Sengupta, 2003).

After the completion of the sorption step, residual materials were re-suspended in a 0.01 M KCl solution to monitor P desorption for the same reaction times as in the sorption step (0.4 to 50 d). There was a negative linear correlation between the soluble P reduction in litter suspensions and the P desorbed (% P sorbed during the sorption step) (Fig. 7). The Al/P molar ratio of the mixtures influenced the amount of P desorbed (Fig. 7). The greater the Al/P molar ratio, the greater the P sorption and the smaller the amount of P desorbed.

Analysis of variance for the desorption step of the central composite design showed that WTR, and alum rates, or reaction time were all significant at the 95% confidence level, but interactions were not significant (data not shown). For alum- or WTR-only treated litter suspensions, $\sim 35\%$ of sorbed P was desorbed into solution after 25 d. This is contrasting to what we found in other P desorption experiments with the same Al-WTR. Minimal (0.2% of sorbed P) concentrations of oxalate (5 mM)-desorbable P were measured in WTR suspensions that were equilibrated for 80 d (Makris, 2004). The difference between the above experiment (0.2% desorbed P) and

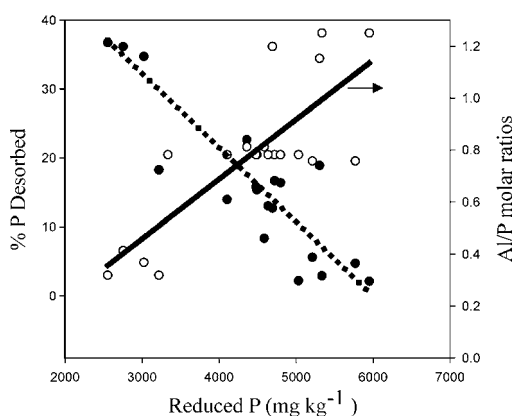


Figure 7. Sorbed P levels as related to (i) desorbed P as a percentage of sorbed P (open circles) and (ii) Al/P molar ratios (closed circles) after the completion of the P desorption in all runs of the central composite design.

the current (35% desorbed P) is the presence of poultry litter in the current study. Somehow, the presence of OC has not only reduced the P sorption effectiveness of the WTR-only and the alum-only treatments but also increased the amounts of P desorbed. Interestingly, the % P desorbed from either sorbent was reduced to less than 1% with increasing Al/P molar ratios close to 1. Competition of phosphate and organic acids for sorption sites is well documented (Eick et al., 1999). It seems that the DOC competes with P for sorption sites only at low number of sorption sites. As sorption sites increase by adding larger sorbent mass, DOC interference with P sorption decreases. The impacts of DOC on P desorption by WTRs is a relevant consideration and warrants additional research.

SUMMARY AND CONCLUSIONS

An Al-WTR and alum were compared individually and as mixtures with respect to efficacy in reducing soluble P in poultry litter. On a per-mole of oxalate-extractable Al basis, the Al-WTR was nearly as effective as alum in reducing P release at a specific pH (6.5). The WTR-only treatment sorbed 22.5 g P kg^{-1} WTR (52% of initial soluble P in untreated litter) after 25 d. The reduced effectiveness of the WTR-only and alum-only treatments was overcome by increasing the molar Al/P ratios of the suspensions. Increases in molar Al/P ratios were achieved by combining sorbent loads that were greater than the loads corresponding to the alum-only or WTR-only treatments. A total of 1–1.3 Al/P molar ratios were adequate to remove all soluble poultry-P, regardless of reaction time.

No significant synergistic or antagonistic effects occurred with combined alum and Al-WTR loads, despite different inferred mechanisms of P sorption by WTRs and alum. Soluble Al and TOC concurrently decreased as P sorption increased, suggesting that at least some of the immobilized P was either in the form of an organo-Al-P amorphous moiety, or very fine colloidal phase. A significant amount ($\sim 35\%$ of sorbed P) of P was desorbed from the WTR-only and alum-only treatments. Dissolved organic carbon was suggested to be an important factor for the large amounts of desorbable P. However, the amount of P desorbed from the mixtures decreased to $< 1\%$ with sorbent loads up to a 1.2 Al/P molar ratios. Greater molar Al/P ratios suggest larger number of sorption sites, i.e., less competition between DOC and P for sorption sites.

Two significant advantages of Al-WTRs compared to alum indicated by this study are cost effectiveness, and significantly less release of dissolved Al. Other data (not shown) suggested that given enough reaction time, different Al-WTRs exhibit similar P sorption characteristics to the Al-WTR used in this study (Makris, 2004). On the other hand, Fe-WTRs were less effective than Al-WTRs, and oxalate-extractable Fe was not a good measure of P sorption capacities of the Fe-WTRs (Makris, 2004).

Additional research is needed to document these advantages at field scale, as well as to determine the effect of DOC on P sorption/desorption from WTR-treated poultry litter.

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